Physically, the $d_{3z^2-r^2}$ mixing has the effect of augmenting the ground-state lobes which are directed along the x axis, while diminishing those along the y axis, or *vice versa*. The negative values of b suggested by the epr data of the vanadyl–benzac complexes means that in these compounds the ground-state lobes along x are augmented, and simple crystal field theory would relate this to a perturbation acting like a negative charge along the y axis. This seems reasonable, as the oxygen hydrid σ orbital which is directed approximately toward the metal atom is probably weighted somewhat more toward the interior than the exterior of the chelate ring. The oxygen orbital involved in the C–O σ bonding is surely directed along the bond, while the one pointing approximately toward the metal ion is probably a hybrid sp^η ($\eta \geq 2$) and so is directed along a line making an angle of 120° or less with the CO bond, whereas the C–O–M angle (ϵ in Figure 1a) is generally ~7° greater than 120° (it is 127.5° in *cis*-VO(benzac)$_2$[3]). Therefore, the ground-state metal orbital lobes along y probably interact more strongly with the occupied ligand σ-bonding orbitals than do those along x.

Acknowledgment.—We wish to thank Dr. Brian Moores for several helpful discussions.

CONTRIBUTION FROM THE CYANAMID EUROPEAN RESEARCH INSTITUTE,
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The Pentacarbonyls of Ruthenium and Osmium. IV. Synthesis of Alkyl- and Acetylosmium Carbonyls

BY F. L'EPLATTENIER[1]

Received November 4, 1968

The sodium salt Na[OsH(CO)$_4$] has been obtained in high yields by the reduction of OsH$_2$(CO)$_4$ with sodium sand in tetrahydrofuran. The nuclear magnetic resonance and infrared spectra are in agreement with a symmetry C_{3v} and a metal–hydrogen bond. No evidences for the formation of the dianion Os(CO)$_4^{2-}$ were obtained. The monosodium derivative is a strong nucleophilic reagent and reacts with methyl halides to give the new alkyl compounds OsCH$_3$H(CO)$_4$, OsCH$_3$I(CO)$_4$, and Os(CH$_3$)$_2$(CO)$_4$. Nmr and infrared spectra indicate a *cis*-octahedral structure for all three substances. Methylhydridotetracarbonylosmium could not be isolated in a pure state; at room temperature it decomposes very rapidly with evolution of methane. On addition of triphenylphosphine, the decomposition is promoted; Os(CO)$_4$P(C$_6$H$_5$)$_3$ and Os(CO)$_3$(P(C$_6$H$_5$)$_3$)$_2$ are formed, together with some monosubstituted OsCH$_3$H(CO)$_3$P(C$_6$H$_5$)$_3$. The two other alkyl derivatives OsCH$_3$I(CO)$_4$ and Os(CH$_3$)$_2$(CO)$_4$ seem to be thermally very stable. The reaction of OsBr$_2$(CO)$_4$ with methylmagnesium bromide was also investigated. The salt [MgBr]$_2$[Os(COCH$_3$)$_2$Br$_2$(CO)$_2$]·5THF was obtained. Infrared and nmr data suggest an all-*cis* configuration for the anion Os(COCH$_3$)$_2$Br$_2$(CO)$_2^{2-}$.

We have recently reported[2] the synthesis and the identification by nuclear magnetic resonance and infrared spectroscopy of dihydridotetracarbonylosmium, OsH$_2$(CO)$_4$, and some of its substitution products. In the triad Fe, Ru, and Os, very few alkylcarbonyls are known and those of osmium seem to have been completely neglected. This prompted us to carry out the reduction of OsH$_2$(CO)$_4$ with sodium and to investigate the reactivity of the so formed monoanion OsH(CO)$_4^-$ toward methyl bromide and methyl iodide. The following new compounds were identified: methylhydridotetracarbonylosmium, OsCH$_3$H(CO)$_4$, methyliodotetracarbonylosmium, OsCH$_3$I(CO)$_4$, and dimethyltetracarbonylosmium, Os(CH$_3$)$_2$(CO)$_4$.

We also studied the reaction of dibromotetracarbonylosmium, OsBr$_2$(CO)$_4$, with methylmagnesium bromide and isolated the diacetyl anion Os(COCH$_3$)$_2$Br$_2$(CO)$_2^{2-}$. This anionic metal complex is closely related to the anionic alkylmetal carbonyls of the type M(CO)$_5$COR$^-$ (M = Cr, Mo, W) synthesized by Fischer and Maasböl.[3,4]

Experimental Section

All of the preparations described in this paper were carried out under an atmosphere of prepurified nitrogen.

Osmium tetroxide was purchased from Johnson Matthey Chemicals Ltd., London. Hydrogen was analytical grade and carbon monoxide was reagent grade and used without further purification. Tetrahydrofuran was treated with iron(II) sulfate and distilled over sodium and lithium tetrahydridoaluminate. Triphenylphosphine was sublimed before use.

The high-pressure reactions were carried out in a 200-ml stainless steel autoclave, heated in a thermostated oil bath.

The infrared spectra were measured with a Perkin-Elmer instrument, Model 521, equipped with grating. The spectra were recorded on an expanded abscissa scale and calibrated with CO. The limit of accuracy based on instrument specifications and reproducibility of data is believed to be ± 1 cm^{-1}.

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[1] Department of Chemistry, University of Neuchâtel, 2000 Neuchâtel, Switzerland.

[2] F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, **6**, 2092 (1967).

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TABLE I

INFRARED DATA OF OSMIUM CARBONYL DERIVATIVES

Compound	ν_{CO}, cm^{-1}	ν_{M-H}, cm^{-1}	Solvent
$Na[OsH(CO)_4]$	2010 s, 1949 s, 1881 vs[a]	1848 s[b]	THF
$OsCH_3H(CO)_4$[c]	2135 w, 2063 m, 2042 vs, 2028 s	1951 vw[b]	THF
$OsH_2(CO)_4$[d]	2139 w, 2067 m, 2055 s, 2047 vs	1938 w	C_6D_6
$OsCH_3I(CO)_4$	2147 w, 2072 vs, 2027 s		Heptane
	2151 w, 2071.5 vs, 2030.5 s		THF
$Os(CH_3)_2(CO)_4$	2130 w, 2044.5 vs, 2012 s		Heptane
	2131 w, 2041 vs, 2007 s		THF
$Os(CH_3)_2(CO)_3P(C_6H_5)_3$	2070.5 vs, 1998.5 vs, 1964 s		Heptane
$[MgBr]_2[Os(COCH_3)_2Br_2(CO)_2]\cdot 5THF$	2022 s, 1935 vs, 1552 m[e]		THF

[a] This band is broad and asymmetric. [b] The attribution of these bands to metal–hydrogen stretching vibrations is uncertain (see text). [c] Not isolated in a pure state. The bands due to $Os(CH_3)_2(CO)_4$ have been subtracted. [d] Data from ref 2. [e] This band is attributed to the ketonic C–O stretching vibration.

TABLE II

NMR DATA OF OSMIUM CARBONYL DERIVATIVES

Compound	Solvent	Chem shift,[a] τ, ppm	Multiplicity	$J_{CH_3,H}$, cps	$J_{CH_3,P}$, cps	Integrated area	Assignment
$Na[OsH(CO)_4]$	THF	20.24, 20.62[b]	1, 1				Os–H
$OsCH_3H(CO)_4$[c]	THF	10.00	2	2.4		3	Os–CH_3
		17.94	4	2.4		1	Os–H
$OsCH_3H(CO)_3P(C_6H_5)_3$[d]	THF	10.23, 10.37	2, 2	2.4	8.5		Os CH_3
$OsCH_3I(CO)_4$	$CD_3C(=O)CD_3$	9.22	1				Os–CH_3
$Os(CH_3)_2(CO)_4$	THF	9.95	1				Os–CH_3
$Os(CH_3)_2(CO)_3P(C_6H_5)_3$	$CD_3C(=O)CD_3$	2.40–2.85	Complex pattern			15	Phenyl hydrogens
		9.86	1		..	3	Os–CH_3
		10.23	2		8.4	3	Os–CH_3
$[MgBr]_2[Os(COCH_3)_2Br_2(CO)_2]\cdot 5THF$	$CD_3C(=O)CD_3$	6.37, 8.21	Complex pattern			40	THF hydrogens
		7.39, 7.63	1, 1			6	Os–$C(=O)CH_3$

[a] From tetramethylsilane as internal reference. [b] Peak not always observed in the solutions of $Na[OsH(CO)_4]$. [c] Not isolated in a pure state. The signals due to $Os(CH_3)_2(CO)_4$ and $OsH_2(CO)_4$ have been subtracted. [d] Not isolated. The coupling constant $J_{H,P}$ could not be determined (see text).

Nuclear magnetic resonance spectra were measured at room temperature on a Varian Model DP60/A. Microanalyses were by Mr. A. Bernhardt, Elbach über Engelskirchen, Germany.

(1) $Na[OsH(CO)_4]$ and $[Ni(phen)_3][OsH(CO)_4]_2$.—Osmium tetroxide (0.602 g, 2.37 mmol) was introduced into the autoclave together with tetrahydrofuran (30 ml). Carbon monoxide and hydrogen in a 3:1 ratio were then compressed to a total pressure of 180 atm. The autoclave was heated to 160° for about 12 hr. After cooling to room temperature, the gases were vented and the volatile $OsH_2(CO)_4$, together with the solvent, was then condensed *in vacuo* under exclusion of light into a flask maintained at Dry Ice temperature. Sodium sand (0.110 g, 4.78 mg-atoms) was added to this colorless solution of $OsH_2(CO)_4$. After 4 hr of stirring at room temperature, the conversion into $Na[OsH(CO)_4]$ was almost quantitative, as inferred by the low intensities of the carbonyl bands due to unreacted dihydride. No infrared evidence for the presence of a dianion such as $Os(CO)_4^{2-}$ was obtained. The yellow reaction mixture was filtered to eliminate the excess of sodium sand and evaporated to dryness. A yellow residue which began to crystallize at 0° was isolated. The latter was redissolved in 10 ml of distilled water and slowly precipitated with 20 ml of a 0.1 *M* solution of nickel(II) *o*-phenanthroline. A yellow-brown solid precipitated out. After filtration, the residue on the filter was washed four times with 15 ml of water and dried under high vacuum at room temperature for 24 hr (64% yield). *Anal.* Calcd for $C_{44}H_{26}N_6NiO_8Os_2$: C, 43.83; H, 2.17; N, 6.97; Ni, 4.87. Found: C, 43.55; H, 2.23; N, 6.82; Ni, 5.04. The infrared and nmr data of $Na[OsH(CO)_4]$ are reported in Tables I and II.

(2) Reaction of $Na[OsH(CO)_4]$ with CH_3I.—(a) To a tetrahydrofuran solution (15 ml) of $Na[OsH(CO)_4]$ prepared from 1.635 g (6.44 mmol) of osmium tetroxide according to section 1, 0.4 ml (6.4 mmol) of methyl iodide was slowly added at 0° under vigorous stirring. After 20 min at room temperature, the volatile components of the reaction mixture, together with the solvent, were condensed *in vacuo* into a flask maintained at Dry Ice temperature. In the nmr spectrum of this condensate, the following signals were observed: two large peaks, one at τ 9.22 ($OsCH_3I(CO)_4$, *vide infra*) and another at τ 9.82 (methane), a smaller peak at τ 9.95 ($Os(CH_3)_2(CO)_4$, *vide infra*), and a small peak at τ 18.84 ($OsH_2(CO)_4$[2]). The most volatile components of this reaction mixture, as well as the solvent, were eliminated through evaporation *in vacuo*, which leaves 0.830 g (29% yield, based on osmium tetroxide) of a yellowish crystalline product. Two successive recrystallizations from heptane and sublimations at room temperature (10^{-1} mm) gave colorless crystals of pure $OsCH_3I(CO)_4$. *Anal.* Calcd for $C_5H_3IO_4Os$: C, 13.52; H, 0.68; I, 28.57. Found: C, 13.61; H, 0.72; I, 28.59; mp 105–106° dec. The infrared and nmr data of $OsCH_3I(CO)_4$ are reported in Tables I and II and in Figure 1.

(b) In another experiment a tetrahydrofuran solution (5 ml) of $Na[OsH(CO)_4]$, prepared from osmium tetroxide (0.933 g, 3.67 mmol), was allowed to react under conditions similar to those described in section 2a, with 0.1 ml (1.6 mmol) of methyl iodide. In the nmr spectrum of the tetrahydrofuran solution of the volatile reaction products, beside the signals mentioned above, a doublet centered at τ 10.00 and a quartet at τ 17.94 in the ratio 3:1 (see Table II) attributed to $OsCH_3H(CO)_4$ were

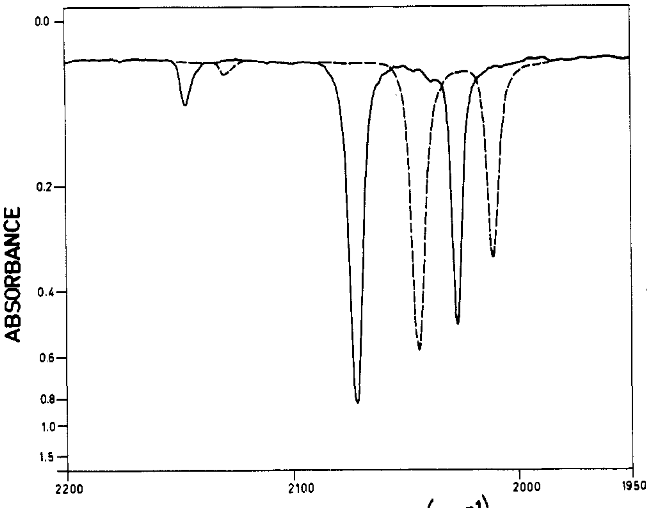

Figure 1.—Infrared spectra of osmium alkyls in heptane solutions using a 0.1-mm cell: ——, $OsCH_3I(CO)_4$; - - - -, $Os(CH_3)_2(CO)_4$.

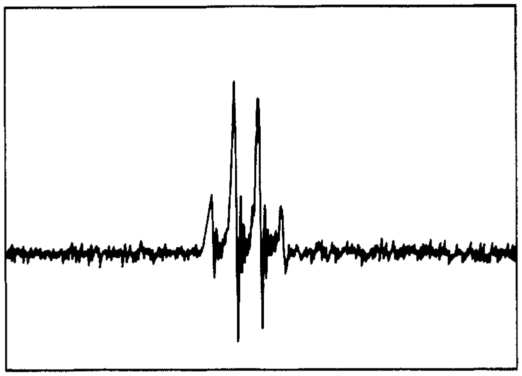

Figure 2.—Nuclear magnetic resonance signal centered at τ 17.94, with $J_{\mathrm{CH_3,H}} = 2.4$ cps, for the hydridic hydrogen of $OsCH_3H(CO)_4$ in tetrahydrofuran. Internal reference, TMS.

observed. This time, the signals of $OsCH_3I(CO)_4$ and CH_4 were much smaller. $OsCH_3H(CO)_4$, which is probably a liquid at room temperature, could not be isolated in a pure state; it decomposes at room temperature with evolution of methane. The addition of triphenylphosphine promotes the decomposition to $Os(CO)_4P(C_6H_5)_3$ and $Os(CO)_3(P(C_6H_5)_3)_2$. Nmr evidence for the formation of a monosubstituted derivative $OsCH_3H(CO)_3P(C_6H_5)_3$ could however be obtained. Attempts to isolate the latter compound were unsuccessful. Infrared and nmr data are in Tables I and II and in Figures 1 and 2.

(3) Reaction of $Na[OsH(CO)_4]$ with CH_3Br.—To a tetrahydrofuran solution (20 ml) of $Na[OsH(CO)_4]$ prepared from 1.702 g (6.70 mmol) of osmium tetroxide according to section 1, a solution of methyl bromide (6.70 mmol) in diethyl ether was slowly added at 0°, under vigorous stirring. The resulting reaction mixture was allowed to warm up to room temperature. The stirring was continued for 20 min. The volatile components were evaporated *in vacuo* together with the solvent and condensed into a flask maintained at Dry Ice temperature. An nmr spectrum of the volatile reaction products showed the presence of $OsCH_3H(CO)_4$ and a peak at τ 9.95 ($Os(CH_3)_2(CO)_4$, *vide infra*), beside some dihydridotetracarbonylosmium. No resonance signals for methane or $OsCH_3Br(CO)_4$ were observed. The condensate was treated with 0.879 g (3.35 mmol) of triphenylphosphine for 4 hr at room temperature. The reaction mixture was distilled under vacuum. The nmr spectrum of the distillate, which is believed to be pure $Os(CH_3)_2(CO)_4$, had only one resonance signal at τ 9.95. The corresponding infrared spectrum is in Table I and Figure 3. Dimethyltetracarbonylosmium, which is probably a solid at room temperature, could not be isolated because of its high volatility and was converted into its substitution product with triphenylphosphine by the following procedure. An approximately stoichiometric amount of triphenylphosphine was added to a tetrahydrofuran solution of $Os(CH_3)_2(CO)_4$. The solution was heated for 4 days at 70°. After this reaction time, an infrared spectrum indicated a conversion of about 50%. The reaction mixture was evaporated to dryness and dried under high vacuum to eliminate the unreacted $Os(CH_3)_2(CO)_4$. After three successive recrystallizations from heptane to eliminate the excess of triphenylphosphine, a small yield of pure $Os(CH_3)_2(CO)_3P(C_6H_5)_3$ as colorless crystals was obtained. *Anal.* Calcd for $C_{23}H_{21}O_3OsP$: C, 48.76; H, 3.74; P, 5.47. Found: C, 48.59; H, 3.62; P, 5.65. The infrared and nmr data of this compound are in Tables I and II.

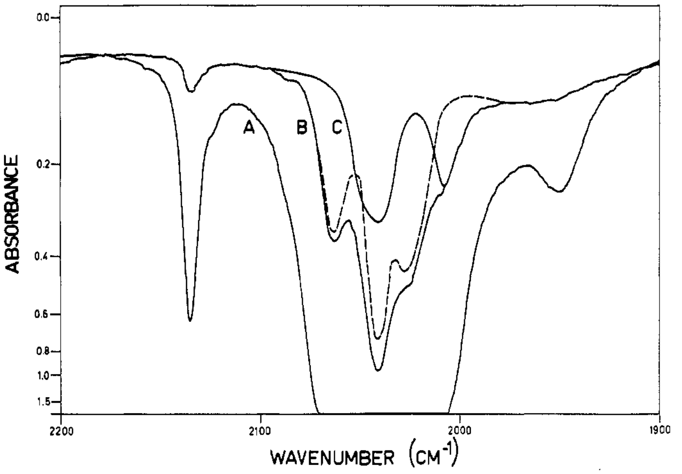

Figure 3.—(A) Infrared spectrum of the volatile reaction products obtained by the reaction of CH_3Br with $Na[OsH(CO)_4]$ using tetrahydrofuran and a 0.1-mm cell. (B) Infrared spectrum A diluted. (C) Infrared spectrum of $Os(CH_3)_2(CO)_4$ using tetrahydrofuran and a 0.1-mm cell. The dashed line indicates the calculated infrared spectrum of $OsCH_3H(CO)_4$ from spectrum B, after elimination of the absorption bands of $Os(CH_3)_2(CO)_4$.

(4) $[MgBr]_2[Os(COCH_3)_2Br_2(CO)_2]\cdot 5THF$.—To a tetrahydrofuran solution (50 ml) of dibromotetracarbonylosmium (0.504 g, 1.09 mmol), synthesized from dihydridotetracarbonylosmium and carbon tetrabromide,[2] the methyl Grignard reagent (3.4 ml of a 0.65 *M* solution), prepared from methyl bromide and magnesium in diethyl ether, was added very slowly under vigorous stirring at 0°. After 1 hr, no absorption bands of unreacted dibromotetracarbonylosmium were observed in the infrared spectrum of the light yellow reaction mixture. After evaporation to dryness, the yellow residue was redissolved in 20 ml of tetrahydrofuran and 3 ml of heptane was slowly added. During about 1 week at −80°, colorless crystals precipitated out. These were decanted, washed once with cold tetrahydrofuran and twice with heptane, and dried for 48 hr at 20° (10^{-3} mm). Substantially pure product was obtained in 34% yield. *Anal.* Calcd for $C_{26}H_{46}Br_4Mg_2O_9Os$: C, 29.43; H, 4.37; Br, 30.12. Found: C, 29.26; H, 4.32; Br, 29.83. Nmr and infrared data are in Tables I and II.

Results and Discussion

Reduction of Dihydridotetracarbonylosmium.—In the present investigation, the easy preparation of $OsH_2(CO)_4$[2] prompted us to select this dihydride as starting material for the synthesis of anions of osmium carbonyl. The reductions were performed with sodium sand in an inert solvent such as tetrahydrofuran. Under such reaction conditions, the sodium salt $Na[OsH(CO)_4]$ was obtained with no evidence for the formation of the dianion $Os(CO)_4^{2-}$. The existence of this monoanion in these solutions was further demonstrated by the isolation, in high yield, of the tris(*o*-phenanthroline)nickel(II) complex $[Ni(phen)_3][OsH(CO)_4]_2$.

Some years ago Thomas published the spectra of hydrido- and deuteridotetracarbonylferrate anions in various solvents.[5] The spectra are consistent with a trigonal-bipyramidal arrangement of C_{3v} symmetry and a metal–hydrogen bond. The infrared absorption bands at 2015 (m), 1937 (s), and 1886 (vs) cm^{-1} in water were assigned to the three C–O stretching vibrations, while the band at 1832 cm^{-1}, shifted to 1336 cm^{-1} in the deuterido derivative, was assigned to the metal–hydrogen stretching vibration. The hydridotetracarbonylosmate anion gave essentially the same spectrum (Table I). The geometrical structure of $OsH(CO)_4^-$ is therefore expected to be similar to that of the iron derivative, with the hydrogen atom lying on the C_3 axis. The assignment of the band at 1848 cm^{-1} to an osmium–hydrogen stretching vibration is uncertain however for, as suggested by Edgell and coworkers with sodium tetracarbonylcobaltate,[6] such anions are subjected to strong interaction with the environment, with the resulting appearance of unexpected bands in the infrared spectrum. These "extra" bands are due to the formation in pure tetrahydrofuran of ion pairs, such as $Na^+Co(CO)_4^-$, the close proximity of the sodium ion distorting the effective electrical symmetry of $Co(CO)_4^-$.

In the nmr spectrum of $Na[OsH(CO)_4]$ (tetrahydrofuran) a sharp signal at τ 20.24 was observed. On acidification this peak was shifted to τ 18.84, the position characteristic for $OsH_2(CO)_4$.[2] A second smaller peak at τ 20.62 was sometimes observed in the nmr spectrum of these solutions. The latter was also shifted to τ 18.84 on acidification. Though the exact nature of this by-product was not elucidated, this signal could be due to the presence of another geometrical isomer of $OsH(CO)_4^-$.

When the light yellow tetrahydrofuran solution of $OsH(CO)_4^-$ was allowed to stand a few days at daylight, it became red, even in the absence of oxygen, and the nmr signal at τ 20.24 diminished slowly. This behavior may be explained by the formation of a dimer or some higher homologs with loss of hydrogen. Wender and coworkers[7] mentioned an analogous behavior for $FeH(CO)_4^-$ which dimerizes to $Fe_2(CO)_8^{2-}$ with evolution of hydrogen.

Osmium Alkyls. Formation and Reactivity.—The sodium salt $Na[OsH(CO)_4]$ behaves as a strong nucleophile and reacts readily with methyl halides to give the alkyl derivatives $OsCH_3H(CO)_4$, $Os(CH_3)_2(CO)_4$, and $OsCH_3I(CO)_4$ as well as CH_4, $OsH_2(CO)_4$ and $OsI_2(CO)_4$. The formation of these different reaction products may be best explained as

$$\begin{tikzcd}
\mathrm{Na[OsH(CO)_4]+CH_3X} \arrow[rr, "1"] & & \mathrm{OsCH_3H(CO)_4+NaX} \arrow[dl, "\mathrm{CH_3I}"', "2"] \arrow[dr, "\mathrm{Na[OsH(CO)_4]}", "4"'] & & \mathrm{(X=Br,\ I)} \\
& \mathrm{OsCH_3I(CO)_4 + CH_4} \arrow[d, "\mathrm{CH_3I}"', "3"] & & \mathrm{Na[OsCH_3(CO)_4] + OsH_2(CO)_4} \arrow[d, "\mathrm{CH_3X}"', "5"] & \\
& \mathrm{OsI_2(CO)_4 + CH_3CH_3} & & \mathrm{Os(CH_3)_2(CO)_4 + NaX} &
\end{tikzcd}$$

Path 1 describes the expected reaction of the nucleophile $Na[OsH(CO)_4]$ toward reagents such as organic halides. The so formed $OsCH_3H(CO)_4$ is unstable in the presence of CH_3I and reacts to give $OsCH_3I(CO)_4$ with evolution of methane, characterized by a peak at τ 9.82 (tetrahydrofuran) in the nmr spectrum. By route 3 $OsCH_3I(CO)_4$ may react with another mole of CH_3I to give *cis*-$OsI_2(CO)_4$ and ethane. The amount of diiodotetracarbonylosmium was, however, very small under the reaction conditions described in the Experimental Section. The C–O stretching vibrations of *cis*-$OsI_2(CO)_4$ are at 2163 (m), 2099 (vs), 2084 (s), and 2049 (s) cm^{-1} in heptane. These reactions may be related to the reaction of $OsH_2(CO)_4$ with carbon tetrachloride and carbon tetrabromide, the two hydrogens being replaced by the halogen ligands, to form $OsCl_2(CO)_4$ and $OsBr_2(CO)_4$, respectively.[2]

If methyl bromide, even in excess, was used instead of methyl iodide, no $OsCH_3Br(CO)_4$, $OsBr_2(CO)_4$, or CH_4 was observed in the reaction mixture. $OsCH_3H(CO)_4$, $Os(CH_3)_2(CO)_4$, and $OsH_2(CO)_4$ were the only volatile reaction products isolated. The decreasing nucleophilicity of bromide compared to iodide may explain why $OsCH_3Br(CO)_4$ was not obtained, under the reaction conditions where $OsCH_3I(CO)_4$ was formed.

Dimethyltetracarbonylosmium may be generated as indicated above. $OsH(CO)_4^-$ abstracts a proton from $OsCH_3H(CO)_4$ to give $OsH_2(CO)_4$ and $OsCH_3(CO)_4^-$, which reacts with another molecule of CH_3X to give the very stable $Os(CH_3)_2(CO)_4$.

The instability of $OsCH_3H(CO)_4$ in the presence of strong nucleophiles is also illustrated by its reaction with triphenylphosphine

$$\begin{tikzcd}
\mathrm{OsCH_3H(CO)_4} \arrow[r, "\mathrm{P(C_6H_5)_3}", "6"'] \arrow[dr, "\mathrm{P(C_6H_5)_3}", "8"'] & \mathrm{Os(CO)_4P(C_6H_5)_3 + CH_4} \arrow[r, "\mathrm{P(C_6H_5)_3}", "7"'] & \mathrm{Os(CO)_3(P(C_6H_5)_3)_2 + CO} \\
& \mathrm{OsCH_3H(CO)_3P(C_6H_5)_3 + CO} \arrow[r, "\mathrm{P(C_6H_5)_3}", "9"'] & \mathrm{Os(CO)_3(P(C_6H_5)_3)_2 + CH_4}
\end{tikzcd}$$

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[5] J. P. Thomas, Ph.D. Thesis, Purdue University, June 1962.

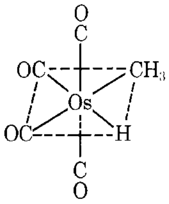
[6] W. F. Edgell, M. T. Yang, and N. Koizumi, *J. Am. Chem. Soc.*, **87**, 2563 (1965).

[7] H. W. Sternberg, R. Markby, and I. Wender, *ibid.*, **79**, 6116 (1957).

On addition of triphenylphosphine to a tetrahydrofuran solution of $OsCH_3H(CO)_4$ and $Os(CH_3)_2(CO)_4$, the doublet at τ 10.00 of $OsCH_3H(CO)_4$ decreased rapidly in intensity, while a pair of new doublets at τ 10.23 and 10.37, attributed to $OsCH_3H(CO)_3P(C_6H_5)_3$ (path 8) appeared. Evolution of methane was also observed. The infrared spectrum of the reaction mixture showed the bands characteristic for $Os(CO)_4P(C_6H_5)_3$[8] (path 6) and $Os(CO)_3(P(C_6H_5)_3)_2$ (paths 7 and 9). Though $OsCH_3H(CO)_3P(C_6H_5)_3$ seems to be somewhat more stable than $OsCH_3H(CO)_4$, attempts to isolate it in a pure state were unsuccessful; recrystallizations cause its decomposition to $Os(CO)_3(P(C_6H_5)_3)_2$.

The reluctance of $Os(CH_3)_2(CO)_4$ to react with triphenylphosphine—4 days at 70° is necessary to obtain a low yield of $Os(CH_3)_2(CO)_3P(C_6H_5)_3$, while $OsH_2(CO)_4$ reacted almost quantitatively to form $OsH_2(CO)_3P(C_6H_5)_3$ after 4 hr at 80°[2]—is probably due to the inductive effect of the methyl groups, which are somewhat poorer electron attractors than hydrogen. This increases the metal–carbonyl bond order and makes substitution of CO groups more difficult.

Infrared and Nmr Spectra.—Though $OsCH_3H(CO)_4$ could not be isolated in a pure state, strong infrared and nmr evidence of its existence and structure are available. The nmr spectrum of $OsCH_3H(CO)_4$ in tetrahydrofuran shows a doublet at τ 10.00 with a coupling constant $J_{CH_3,H} = 2.4$ cps, attributed to the methyl hydrogens, and a quartet at high field (τ 17.94, $J_{CH_3,H} = 2.4$ cps), a position which is characteristic for hydridic hydrogens (see Table II and Figure 2). The ratio between the observed integrated areas for these two different types of hydrogens definitely establishes the presence of one methyl group for each hydridic hydrogen. The infrared spectrum of the volatile reaction products obtained by the reaction of CH_3Br on $Na[OsH(CO)_4]$ is shown in Figure 3. After elimination of the infrared absorption bands of $Os(CH_3)_2(CO)_4$, five absorption bands, which may be attributed to $OsCH_3H(CO)_4$, are left. This is consistent with the formation of the *cis* isomer (structure **1**). A carbonyl derivative of this type, having C_s symmetry, should give rise to four C–O stretching vibrations ($3A' + A''$) and to one metal–hydrogen stretching vibration (A'). By comparison with the spectrum of $OsH_2(CO)_4$ and on intensity grounds, the band at 1951 cm^{-1} may be assigned to a metal–hydrogen stretching vibration.



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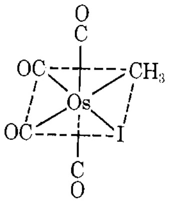

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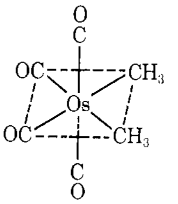

3

The nmr evidence obtained for the formation of a monosubstituted phosphine derivative, $OsCH_3H(CO)_3P(C_6H_5)_3$, substantiates the presence of $OsCH_3H(CO)_4$. Though the exact stereochemistry of the former compound could not be determined, because of its instability, the appearance of a pair of doublets centered at τ 10.30 (tetrahydrofuran) ($J_{CH_3,H} = 2.4$ cps and $J_{CH_3,P} = 8.5$ cps) suggests that the methyl group and the hydridic hydrogen remain *cis* to each other, while the triphenylphosphine enters the *cis* position with respect to the methyl group. In fact, the value of the coupling constant $J_{P,H}$ corresponds to that known for phosphorus and methyl ligands in *cis* position.[9,10] The low concentration of $OsCH_3H(CO)_3P(C_6H_5)_3$ in the reaction mixture did not allow us to measure the coupling constant $J_{P,H}$ in order to determine the relative position of the triphenylphosphine and the hydridic hydrogen in this complex.

For a compound such as $OsCH_3I(CO)_4$ *cis* and *trans* isomers are possible. For the *cis* isomer (structure **2**) of C_s symmetry four infrared-active C–O stretching modes ($3A' + A''$) are again expected. One A' mode associated with the *trans* pair of carbonyls should give rise to a weak band, while the three other modes are expected to have roughly comparable intensities.[11] For the *trans* isomer with C_{4v} symmetry, two infrared-active C–O stretching vibrations are allowed: a strong degenerate E mode and a less intense A_1 mode, due to the symmetrical breathing of the four equatorial CO groups. The spectrum of $OsCH_3I(CO)_4$ in heptane is represented in Figure 1 and Table I and shows only three well-resolved bands. This suggests the presence of the *cis* isomer and an accidental degeneracy of two stretching modes. The strongest band at 2072 cm^{-1} does probably consist of two bands close together, which explains the intensity difference of this band as compared to the band at 2027 cm^{-1}. A similar spectrum was also reported for *cis*-$FeI_2(CO)_4$,[12] where the fourth peak is believed to be coincident with the strongest one, since this is much stronger than the corresponding peaks for the chloride and bromide derivatives.

The nmr spectrum of $OsCH_3I(CO)_4$ shows a single peak at τ 9.22. This signal for the hydrogens of the methyl group is lower than in $OsCH_3H(CO)_4$, where the absorption of the methyl hydrogens was observed at τ 10.00. This may be due to the presence of the electronegative iodide.

As represented in Tables I and II, and in Figures 1 and 3, the infrared and nmr spectra of the substance, supposed to be $Os(CH_3)_2(CO)_4$, are very similar to those of $OsCH_3I(CO)_4$. The probable coincidence of two vibration modes gives again a spectrum with only three well-resolved bands; the relative intensities of the latter are comparable to those obtained for $OsCH_3I(CO)_4$. The two methyl groups are therefore believed to be in a *cis* position (structure **3**). The C–O stretch-

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[8] F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, **7**, 1290 (1968).

[9] C. S. Kraihanzel and P. K. Maples, *J. Am. Chem. Soc.*, **87**, 5267 (1965).

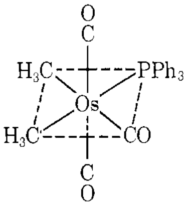
[10] J. P. Collman and C. T. Sears, *Inorg. Chem.*, **7**, 27 (1968).

[11] E. W. Abel and I. S. Butler, *Trans. Faraday Soc.*, **63**, 45 (1967).

[12] K. Noack, *Helv. Chim. Acta*, **45**, 1847 (1962).

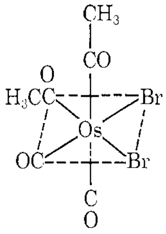
ing frequencies are somewhat lower in the dimethyl derivative. The more electronegative iodide is a better remover of charge from the central metal atom than the methyl ligand. The resulting C–O bond order is therefore lower in $Os(CH_3)_2(CO)_4$, giving rise to lower stretching frequencies. As expected, one sharp signal is observed in the nmr spectrum at τ 9.95, a position which is comparable to that for the methyl hydrogens of $OsCH_3H(CO)_4$.

The nmr and ir features of the reaction product of $Os(CH_3)_2(CO)_4$ with triphenylphosphine (Tables I and II) confirm our first conclusions about $Os(CH_3)_2(CO)_4$. Three infrared-active C–O stretching vibrations are present as expected for a monosubstituted derivative, such as $Os(CH_3)_2(CO)_3P(C_6H_5)_3$. The nmr spectrum with a singlet at τ 9.86 and a doublet centered at τ 10.23 ($J_{CH_3,P} = 8.4$ cps) of equal intensity indicates that the two methyl groups are not equivalent with respect to the phosphorus, one being *cis* and the other *trans*. The only structure which is in agreement with both the nmr and the infrared data is **4**. The ratio between the observed integrated areas for the different types of hydrogens present in this derivative also establishes the presence of two methyl groups in this molecule and consequently in the parent *cis*-$Os(CH_3)_2(CO)_4$. The doublet at τ 10.23 may be attributed to the methyl group *cis* to the phosphorus according to the coupling constant $J = 8.4$ cps, while the methyl group *trans* to the phosphorus would remain unsplit. Schrauzer and Windgassen[13] have reported the value of 4 cps for the coupling constant $J_{CH_3\text{-}Co\text{-}P}$ in tributyl- and triphenylphosphine-substituted methylcobaloximes, where the alkyl group and the phosphorus are *trans* to each other. In our compound the coupling seems to be even smaller, so that the splitting is no more observed.

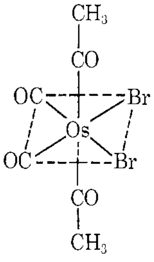


4

Osmium Acetyl.—The reaction of *cis*-dibromotetracarbonylosmium with methylmagnesium bromide gives a diacetyl anion of composition $Os(COCH_3)_2Br_2(CO)_2^{2-}$. Although more complicated mechanisms may be thought of, based on alkylation followed by methyl migration,[14] it is believed that in this case the attack by the Grignard reagent occurs directly on the carbon atom of the carbonyl groups, without breaking of the original metal–halogen bonds. With the two bromides being *cis*, as in the starting material, three geometrical isomers are still possible for such a derivative, namely **5**–**7**. The nmr spectrum, showing two singlets of equal intensity at τ 7.39 and 7.63, suggests the presence of two nonequivalent acetyl groups. Structures **6** and **7** are therefore to be excluded. We are therefore left with structure **5**, which is also in agreement with the infrared spectrum (Table I), namely, two C–O stretching vibrations of comparable intensity. For the C–O stretching vibration of the acetyl groups only one relative broad band was observed at 1552 cm^{-1}. The low wave number for this ketonic C–O stretching vibration, which is analogous to the value obtained for the acetyl group of Li[Mn(COCH$_3$)I(CO)$_4$],[15] namely, 1566 cm^{-1}, is certainly due to some transfer of negative charge to the acetyl groups. The presence of the electronegative bromide ligands prevents however a complete delocalization of the anionic charge to the oxygen atom, as it is known for the complexes $M(CO)_5COR^-$ (M = Cr, Mo, W).[3,4]



5



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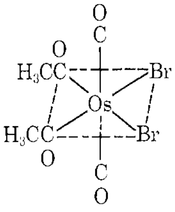

7

Acknowledgment.—The author wishes to thank Dr. F. Calderazzo for helpful discussions and Miss C. Pelichet for technical assistance.

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(13) G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, **88**, 3738 (1966).

(14) K. Noack and F. Calderazzo, *J. Organometal. Chem.* (Amsterdam), **10**, 101 (1967).

(15) F. Calderazzo and K. Noack, *ibid.*, **4**, 250 (1965).